

## CAUSTIC WASHING FOR REFINING OF DIRECT COAL LIQUEFACTION PRODUCTS

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### INTRODUCTION

Extensive research and development sponsored by the U.S. DOE/PETC over the past two decades has resulted in dramatic improvements in the quality of direct coal liquefaction products. High-quality coal-derived distillates are obtainable from catalytic two-stage liquefaction (TSL) processes, such as those developed at the Wilsonville, AL pilot plant and the Hydrocarbon Technologies Inc. (HTI) pilot plant and bench units. The products of the Wilsonville and HTI TSL operations are suitable as high quality feedstocks for producing transportation fuels in a refinery. These products have important quality advantages over crude petroleum: they are distillates boiling below about 700°F and are thus virtually free of resid and metals, and they have very low sulfur contents and low nitrogen contents.<sup>1-3</sup> The coal liquids have carbon and hydrogen contents and Watson characterization factors within the range of crude petroleum.<sup>1-3</sup> However, relative to crude petroleum, the crude coal products have elevated oxygen contents.<sup>1-3</sup> Although these oxygenated species are found at elevated concentrations throughout the boiling range of the coal liquids, they are most frequently concentrated in the heavy naphtha and light kerosene fractions. For example, when the oxygen content of coal liquids is plotted as a function of boiling point, there is often a maximum in the curve between 355 °F and 465 °F (Figure 1 and References 1, 2, and 4).

Phenolic compounds are the predominant oxygen-containing components in the coal liquids;<sup>4</sup> the curve maximum represents phenols with zero to three alkyl carbon substituents. Phenolic compounds must be reduced to low concentrations to produce finished transportation fuels. In a typical modern petroleum refining scheme, this would be accomplished by hydrotreating. However, because coal liquids have high concentrations of phenolics, it may be advantageous to reduce their concentration prior to hydrotreating by some other route, for example, by caustic extraction. Although caustic washing could not replace hydrotreating to produce finished fuels from the oils described here, this route for pre-removal of phenols could have several advantages over hydrotreating the phenolic containing oils: it would reduce the overall hydrogen demand, it could produce a valuable by-product (cresylic acid), and it would simultaneously strip from the oil mercaptans and hydrogen sulfide in addition to the phenolics. Indeed, caustic washing was once a common unit operation in petroleum refineries because of its ability to sweeten light distillates.<sup>5</sup> The cresylic acid could be sold as a by-product or perhaps methylated to produce methyl aryl ethers,<sup>6</sup> which could be used as a high octane oxygenate gasoline extender. Presented here are results of experiments conducted to recover a cresylic acid by-product from crude coal liquids, while simultaneously improving the quality of the liquid. The quality improvement in the coal liquid and the characterization of the by-product cresylics are discussed.

### EXPERIMENTAL

The net products of three liquefaction runs that represent variations of state-of-the-art technology were characterized in detail. The three samples were generated at the Wilsonville 6 ton/day pilot plant (Run 2600) and the HTI 2 lb/hr bench unit (Runs CC-15 and CMSL-2), as described in Table 1. The characterization scheme included fractional distillation and analysis and inspection of the fractions. Some of the distillation fractions were caustic washed to remove phenolics and the recovered raffinate and caustic extract fractions were also characterized. The exact caustic washing procedure used varied among the samples; however, the general scheme was to contact the oil in a separatory funnel multiple times with NaOH (either 20 wt % or 6 wt % solutions) then with water, to acidify the extract with concentrated aqueous HCl, then to extract the phenols with methylene chloride and to remove the methylene chloride by rotary evaporation. Raffinate and caustic extract yields are determined gravimetrically. Some losses resulted from evaporation and handling during the extraction scheme. The complete backgrounds of the samples, details of all experimental methods and characterization data appear in the original reports of this work.<sup>7-9</sup> Phenolic -OH concentrations were determined by Fourier-transform infrared spectroscopy.<sup>10</sup> The caustic extracts also were characterized by gas chromatography/mass spectrometry (GC/MS) with a HP 5970 system equipped with a 30 m x 0.25 mm DB-5 column (0.25 µm film thickness) as follows: 20 psig He carrier gas; splitless injection as 1% solutions in THF; injection port at 300 °C; column temperature program - 5 min at 35 °C, to 100 °C at 35 °C/min, to 320 °C at 4 °C/min; scan from 45 to 300 amu; spectra searched against the Wiley/NBS mass spectral library; identifications based on search results and supplemented by

retention times; normalized quantitation is based on peak area divided by total peak area of all phenolics found.

## DISCUSSION

The oxygen contents, determined by difference, of the distillation fractions of the three crude coal liquids are plotted in Figure 1 as a function of the mid boiling point of the fraction. Two of the three curves show maxima between 355 and 465 °F. Material in this boiling range tends to have relatively high concentrations of phenolic compounds. For example, Table 2 shows that the 380-510 °F fraction has the highest phenolic -OH concentration of the four distillation fractions of the Wilsonville Run 260D sample.

The fractions of the Wilsonville Run 260D sample that were caustic washed include the naphtha (IBP-380 °F), Jet or kerosene (380-510 °F), diesel fuel (510-650 °F), and residuum (650 °F) fractions. Table 2 shows the yields of raffinate and extract from each extraction and the phenolic -OH concentration in each fraction. The phenolic -OH concentrations (Table 2) of the raffinates show that caustic washing was quite effective at removing phenolics from the fractions boiling below 510 °F. In fact, for these raffinates, phenolic -OH was near or below detection limits. Caustic washing was not very effective for the higher boiling fractions. Not only was caustic washing less effective for the higher boiling fractions, it was also less selective; GC/MS analyses showed that the caustic extracts of the higher boiling fractions were contaminated with hydrocarbons. For this reason, and because the highest concentration of phenolics tend to exist in fractions that boil between 355 and 465 °F (Figure 1 and References 1, 2, and 4), only the naphtha (IBP-380 °F) and kerosene (380-510 °F) fractions of the HTI Run CC-15 sample and the "swing cut" (350-400 °F) fraction of the HTI Run CMSL-2 sample were caustic washed. The raffinates of the fractions from HTI Runs CC-15 and CMSL-2 were characterized by the same set of inspection tests as the original, unextracted fractions. The caustic extracts of the fractions from all three runs were characterized by GC/MS analysis and phenolic -OH determination.

The caustic extract yields range from 1.1 to 4.6% and losses (100% - yield of raffinate - yield of extract) range from 0.1 to 4.7%. The variations result from the different properties of the fractions, and perhaps from the use of different caustic washing procedures.

Table 3 compares the inspection data of the raffinates with the corresponding data of original, unextracted fractions. For the IBP-380 °F fraction of Run CC-15, the lower Reid vapor pressure of the raffinate appears to result from the loss of light material during the caustic wash. Properties of that fraction that showed improvement from caustic washing include acidity, copper strip corrosion, existent gum, bromine number, basic nitrogen, oxidation stability, heat of combustion, and mercaptan sulfur. The quality of the fraction in terms of its suitability as gasoline are somewhat improved relative to the unextracted fraction. The major improvements in the 380-510 °F fraction of Run CC-15 from caustic washing include acidity and mercaptan sulfur. Other improvements include oxygen (by diff.), viscosity and bromine number.

For the 350-400 °F fraction of HTI Run CMSL-2, the property which showed the greatest improvement from caustic washing is the mercaptan sulfur content. Many other properties (e.g., bromine number, acidity, oxygen by diff.) show some changes that indicate the raffinate is a better stock for production of transportation fuels. The oxidation stability decreased; this may result from the removal of hindered phenols, which are known to act as antioxidants. However, the opposite effect was seen with the IBP-380 °F fraction of HTI Run CC-15, as discussed above.

The major components of the caustic extracts, as determined by GC/MS analysis, are provided in Table 4. Although the extracts of the higher boiling fractions contained some hydrocarbons, each caustic extract consisted primarily of phenolics. The high measured phenolic -OH concentrations of the caustic extracts (Table 2) confirm this. Depending on the boiling point of the fraction extracted, the caustic extracts consist of phenols with zero to four alkyl substituents.

## SUMMARY

Caustic washing was found to be highly efficient and highly selective for the extraction of phenolics from the light distillate fractions (b.pt. <510 °F) of the products of modern two-stage direct coal liquefaction products. The extracts were composed almost entirely of phenolics and the lower boiling raffinates were almost devoid of phenolics. The properties of the raffinates as feedstocks or blendstocks for transportation fuels were moderately improved relative to the unextracted materials. Notable improvements included reduced acidity, mercaptan sulfur, oxygen (by diff.) and copper corrosion; other minor improvements also were seen. The composition of the caustic extracts (cresylic acids) depends on the boiling point of the material extracted, but primarily consists of phenols with zero to four alkyl substituents.

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TABLE 1. SOURCE DATA OF COAL LIQUID SAMPLES

Plant/Run	Feed Coal Seam	Process Description		
		Operating Mode	Catalyst	Reactor Temp., °F
Wilsonville 260D HTI CC-15 HTI CMSL-2	Wyodak and Anderson Wyodak and Anderson Illinois No. 6	Catalytic/Thermal Thermal/Catalytic Catalytic/Catalytic	Shell 324/Fe <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> /Shell 317 Shell 317/Shell 317	790/774 800/775 752-777/795-811

TABLE 2. YIELDS AND PHENOLIC -OH CONCENTRATIONS OF FRACTIONS

Fraction	Yields, wt % of Feed Fraction		Phenolic -OH Concentration, meq/g Sample		
	Raffinate	Caustic Extract	Feed Oil	Raffinate	Caustic Extract
<u>Wilsonville Run 260D</u>					
IBP-380 °F	92.7	3.7	0.40	0.02(a)	-
380-510 °F	94.7	3.6	0.92	0.07(a)	-
510-650 °F	94.4	4.6	0.52	0.27	-
650 °F* - Trial 1	95.4	1.9	0.41	0.28	-
650 °F* - Trial 2	97.9	2.0	0.41	0.31	-
<u>HTI Run CC-15</u>					
IBP-380 °F	92.9	2.4	0.13(b)	(c)	8.90
380-510 °F	92.1	4.0	0.24(b)	(c)	7.49
<u>HTI Run CMSL-2</u>					
350-400 °F	95.4	1.1	(c)	(c)	5.02

- (a) Quantitation is uncertain at these extremely low concentrations  
 (b) Amine signal probably contributing to reported phenolic -OH concentrations  
 (c) Amine observed, no phenolic -OH detected

TABLE 3. INSPECTIONS OF ORIGINAL AND RAFFIANTE FRACTIONS

Property	HTI Run CC-15				HTI Run CMSL-2	
	<380 °F		380-510 °F		350-400 °F	
	Original	Raffinate	Original	Raffinate	Original	Raffinate
Spec. Gravity @ 60 °F (D4502)	0.7798	0.7775	0.8899	0.8882	0.8492	0.8484
API Gravity (calculated)	50.0	50.5	27.5	27.8	35.1	35.3
Elemental Analysis, wt %						
Carbon (D5291)	85.93	86.12	87.12	87.75	86.78	86.86
Hydrogen (D5291)	13.96	13.77	11.77	11.68	12.72	13.06
Sulfur (D3120)	0.03	0.03	0.03	<0.01	0.01	0.01
Nitrogen (D4629)	0.09	0.07	0.33	0.33	0.03	0.02
Oxygen (by diff)	0.00	0.01	0.75	0.23	0.46	0.03
Basic Nitrogen (JOP269)	0.082	0.058	0.274	0.264	0.023	0.023
Mercaptan Sulfur (D3227), ppm	51.5	9.7	45.2	<0.1	19.0	6.0
Viscosity (D445), cSt						
@ 210 °F	-	-	-	-	0.6653	0.8741
@ -20 °C	-	-	10.80	9.665	4.683	4.359
Refractive Index (D1218), @ 20 °C	1.42882	1.42836	1.49196	1.49072	-	-
Freezing Point (D2386), °F	-	-	-12	-13	-99	-95
Cloud Point (D2500), °F	-	-	-	-	<-60	<-60
Pour Point (D97), °F	-	-	-	-	<-60	<-60
Reid Vapor Pressure (D1591), psi	2.54	2.09	<0.01	<0.01	0.02	<0.01
Flash Point (D56, D93), °C	-	-	83	82	50	57
Group Analy. (ASTM D5134 & HC22)						
Paraffins, vol %	38.0	34.7	9.6	9.1	7.5	8.0
Naphthenes, vol %	45.7	48.8	43.1	46.0	61.3	61.5
Aromatics, vol %	8.7	9.2	41.4	41.9	28.4	27.6
Olefins, vol %	4.6	4.2	5.8	3.0	2.6	2.5
Benzene (PIANO, mod D5134)	0.089	0.078	-	-	-	-
Naphthalenes (D1840), vol %	-	-	4.23	3.74	0.48	0.32
Bromine Number (D1159)	3.62	2.37	5.08	2.69	3.00	2.71
Aniline Point (D611), °F	103.8	108.0	71.5	75.2	-	-
Smoke Point (D1322), mm	-	-	10.9	11.6	15.8	15.4
Acidity (D3242), mg KOH/g	0.05	<0.01	0.04	0.01	0.01	<0.01
Copper Corrosion (D130)	3b(dark)	2d(mod)	1a(slight)	1a(slight)	1a(slight)	1a(slight)
Existent Gum (D381), mg/100 mL	11.2	9.0	-	-	6.4	6.2
Oxidation Stability (D525), min	105	1440	-	-	1440	720
Thermal Stability (JFTOT) (D3341)	-	-	Fail	Fail	-	-
Octane No., Motor Method (D2700)	60.7	58.1	-	-	-	-
Octane No., Rarch Method (D2699)	61.6	60.2	-	-	-	-
Heat of Combustion (D2382, D240), Net Btu/lb	16,509	18,651	17,918	18,043	16,401	18,411
Luminometer Number (D1740)	-	-	-	-	27.3	27.0

TABLE 4. COMPOSITIONS OF CAUSTIC EXTRACTS

Component	GC/MS Intensity, as % of Total Phenolic Intensity (No. of Resolved Peaks in Parentheses)				
	Wilsonville Run 260D		HTI Run CC-15		HTI Run CMSL-2
	IBP- 380 °F	380- 510 °F	IBP- 380 °F	380- 510 °F	350-400 °F
phenol	24(1)	0.4(1)	13(1)	-	-
o-cresol	15(1)	1(1)	21(1)	-	1.5(1)
m/p-cresol	31(2)	4(1)	24(1)	0.4(1)	1.5(1)
dimethyl phenol	13(6)	14(6)	21(5)	13(6)	32(5)
ethyl phenols	16(2)	13(3)	17(2)	8(2)	10(2)
C <sub>3</sub> -phenols	1(5)	31(12)	4(6)	51(12)	37(11)
C <sub>4</sub> -phenols	-	16(10)	-	24(12)	17(9)
indanol	-	18(1)	-	4(1)	0.3(1)
dihydroxytoluene	-	1(1)	-	-	-
tetralinol	-	2(1)	-	-	-

Only traces of hydrocarbon contaminants found in IBP-380 °F extracts.  
Some hydrocarbon contaminants found in others.

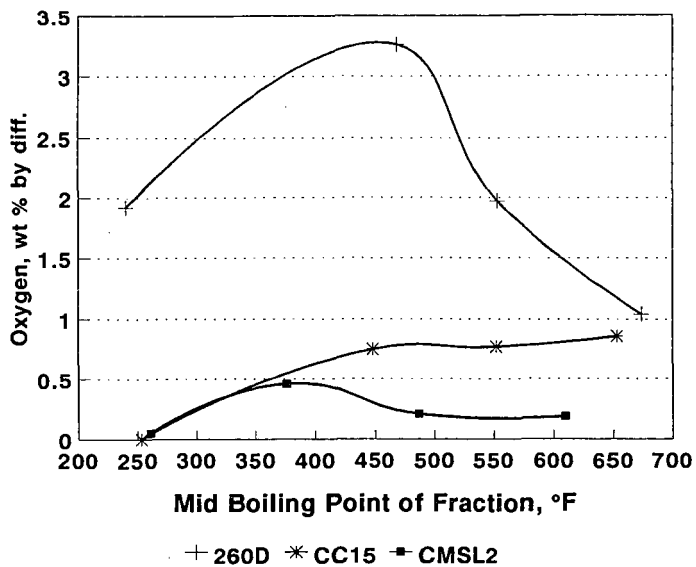


Figure 1. Oxygen Content (by diff.) versus Mid Boiling Point of Coal Liquid Fractions.